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THE MONIST

ON THE FORM AND SPECTRUM OF ATOMS.*

[This article was an address delivered by the author as the official rectorate address in his capacity of Rector Magnificus of the University of Munich. It was published in the original German in the *Süddeutsche Monatshefte* for September, 1905. The present translation, sanctioned and revised by the author, is augmented by additional remarks and diagrams.]

CHEMISTRY teaches that all earthly matter is composed of some seventy so-called elements. The exact number does not concern us here; it will probably increase with the further improvement of our methods of observation. But the fact which claims our attention is that the apparently endless variety of all material phenomena, whether of organic or inorganic nature, are built up from so small a number of different substances—or rather that the number should be limited at all.

In what does the difference between these substances consist? The chemist provides some marks of distinction in his analyses—the color and form of the crystals precipitated by certain reactions, etc. In this way however only the most peculiarly characteristic properties are distinguished. The problem of the intrinsic nature of the different elements remains unsolved. Perhaps we may doubt if this question can be answered at all. In contrast to philosophy, natural science shows only that these distinctions exist, and that there are means by which they may be closely classified. Scientists are content to be limited to

* Translated from the German by Lydia Gillingham Robinson.

this classification; but even if they wished to go further, the line that divides the known from the unknown might perhaps shift its position but could never be removed. Nevertheless it may be profitable to attempt to formulate quantitatively at least the question in regard to the qualitative differences of matter; e. g. to reduce it to the purely geometrical question of form. Of course in analytical geometry every problem of form is easily expressed in terms of quantity, hence we would have the proposition comprehended with mathematical precision, and so at least simplified.

From time immemorial ideas in regard to the actual unity of matter have been generally current. Mechanics and astronomy deal with the concepts of weight and mass only, without having reference to any distinction between the various chemical elements. They presuppose as their foundation the idea of the unity of matter, wherein a common property of all matter is postulated.

The atoms of the chemist are the smallest divisions of matter that can either exist alone or can enter into combination with other atoms. This does not prevent them from being themselves composed of still smaller particles which, however, cannot be isolated. In fact one of the very latest beliefs is that even in this respect a step forward can be made; that a disruption of atoms may actually take place under the influence of electrical forces in the so-called Geisler, or Crookes, or Hittorf tubes; that the so-called cathode rays may prove to be nothing else than the paths of dispersed molecules. Even experiments with the mysterious radium seem to point toward the possibility of so confining these ultimate atoms (*Uratome*) that one element may be changed into another, that out of radium, helium may be produced. The outcome of these experiments is still uncertain, but at least it is incontestable that these latest speculations in physical sci-

ence have succeeded in restoring and popularizing the conviction of the essential unity of all matter.

If the mathematician wishes to handle the proposed question with his own peculiar expedients he must first of all single out of the great variety of chemical properties, one that is accessible to quantitative representation, and which pertains only to the atom and not to groups of atoms such as crystal formations.

Each element has its particular spectrum consisting of a certain number of well-defined lines, by which the element may be positively recognized; i. e., in a gaseous and incandescent state (where the separate atoms circulate freely) each element, and therefore each single atom of the element, emits a light that when observed through the spectroscope does not furnish a continuous many-colored image, as for instance sunlight; but instead, a number of distinct lines whose position can be determined with extraordinary exactness, and each of which corresponds to a quite definite wave length of the particular light-vibration which exactly defines its own color. These wave lengths are numbers, hence quantitative sizes, by means of which all qualitative properties of the element concerned must be fully determined.

From these numbers the mathematician will proceed. He has the following problem before him: In space which is otherwise empty (occupied only by luminiferous ether) floats a material particle from which proceeds a series of vibrations each with clearly defined wave lengths, which are diffused in all directions and become visible as light of definite colors; what properties must this particle possess in order to produce light-vibrations having only these definite wave lengths or groups of wave lengths, and no others? The mathematical treatment is concerned only with the form of the particle and the distribution of matter within it, i. e., the density and elasticity of this matter.

But for such treatment the statement of the question must first be thus reversed: Given a particle of matter of a certain form, density and elasticity, that floats freely in luminiferous ether, what kind of light-vibrations originate from it? i. e., what are the wave lengths of the vibrations peculiar to it (the so-called *Eigenschwingungen*)?

So stated we have to do with a well-defined mathematical problem of the theory of partial differential equations; the matter composing the particle is set in motion (perhaps by contact with other particles); these vibrations continue in the surrounding ether throughout the surface of the particle without in any way interrupting the continuity in the motion of the wave through its surface; by this means is mathematically determined a definite or an infinitely great number of possible wave lengths, which produce an equal number of separate, distinct lines in the spectrum.

We must now vary the density, elasticity, form and size, in order to see whether through these can be reached the empirically established laws of distribution of the spectral lines of certain elements. Unfortunately the mathematical problem is so complicated that it is capable of detailed treatment only for a limited number of cases; and even then the equations are so extraordinarily intricate, that for the most part it must suffice to discuss the mathematical solutions only so far that the general type for the laws of the distribution of spectral lines may become apparent; and many elements too, on the other hand, are sufficiently characterized by this general type.

The simplest possible case is the following: The atom under consideration has the form of a sphere and is composed of matter of a given density and elasticity; what light-waves does this sphere generate? Here the calculation may be carried pretty far; the spectral lines are found to be distributed in the spectrum according to a simpler law than any to which an element has yet been

experimentally found to conform. Although it is enough in many problems of mathematical physics to represent atoms as spherical (especially in most problems of the kinetic theory of gas) yet atoms of an exactly spherical form are hardly ever met with.

Nevertheless the formulas which are valid for the sphere suggest a practically realizable result. When two spheres are composed of matter of equal density and elasticity but differ in size, we have the following law: If the lines of the spectrum for the light emitted by one of the spheres is known, those of the other may be found by multiplying the wave length of the known line by the ratio of the radii of the two spheres. Now if the spheres are of equal density, the ratio of the radii is equal to the cube root of the ratio of the weights of the spheres, or, in other words, the atomic weights of the two elements whose atoms are represented by the spheres. In this form then, the law becomes generally valid: The wave lengths of the spectral lines of two atoms of equal form, density and elasticity, similar to each other and differing only in size, are in the same proportion as the cube roots of their chemical atomic weights. According to this law the lines of one element may be computed from those of the other.

This law may easily be put to a practical test, and for this purpose it is necessary only to compare the spectral lines of different elements in the carefully prepared tables at our disposal. From this it follows that the spectra of the following groups of metals fulfill this law, either entirely or approximately:

1. Zinc, cadmium and mercury.
2. Magnesium, calcium, barium and strontium.
3. Silver, copper and gold.

These are groups of elements which are related in other respects because of their chemical properties. From their atoms we can tell that the elements of each group

are similar to each other; but on the other hand, similarity in chemical relations does not in the least imply similarity in the form of atoms. Proof of this is found in the case of alkalis (lithium, sodium, potassium, caesium, rubidium). The spectral lines of these related elements do not in the least conform to the law above mentioned. What then causes the difference between the three above mentioned groups? Either the atoms are composed of different substances or they are not similar in form.

Let us continue to consider the substance as identical, but vary the form. Instead of a sphere, let us choose first a prolate (that is, almost oval) spheroid, such as is generated geometrically when an ellipse rotates about its long

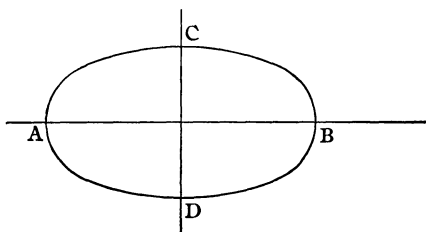


Fig. 1. This ellipse revolving about the axis A B generates a prolate spheroid, revolving about the axis C D an oblate spheroid.

axis. It follows from the mathematical theory that the spectral lines of such an ellipsoid depend on three numbers, that is they can be grouped according to three different principles. These numbers become the roots of certain transcendental equations, and are computed from the lengths of the axes of the ellipsoid, its density and elasticity—a calculation whose actual performance, to be sure, seems hardly practicable.

The first of these three numbers defines a group of related lines, a so-called series; a certain range of such series corresponds to the different possible values of the first number. The second number determines in each series a smaller group of lines, and the third points out in

each subordinate group one single individual line. The way in which the third number enters into the calculation, teaches us further that the reciprocal values of the wave lengths for the single lines of the above mentioned subdivisions, form constant differences among themselves, i. e., differences which depend solely upon the nature of the given ellipsoid. By this means we obtain a characteristic type of line distribution, a type which is familiar to us from the catalogues of spectral lines, and which is to be found only in the case of the above mentioned alkalis. For these Rydberg, Kayser and Runge have derived by observation certain conformities which essentially coincide with those for the spectrum of a prolate spheroid as above described, while the formulas obtained from experiments harmonize according to the type with those obtained from mathematical theory. The latter are derived from the representation of the solutions of linear differential equations by means of semi-convergent series. An actual calculation in all details is of course not possible as yet, because of the complexity of the formulas. The alkali atoms (Li, Na, K, Cs, Rh), we may inversely conclude, have the form of prolate spheroids, and for each single element the axis lengths of these ellipsoids are accurately defined; for different elements of this alkali group the ellipsoids in question are not similar to each other.*

An essentially different line distribution is produced by the so-called oblate spheroid. In this case, too, there are the same number of groups, series and subdivisions, but the law of constant differences becomes less universally valid; the roots of the transcendental equations become in

* The mathematical deduction of this and the following results have been published in two essays in the reports of the *k. bayer. Akademie der Wissenschaften*, Bd. 31-33 (1901-1903). The deduction of the more exact formulas by the aid of the semi-convergent series, as well as the consideration of the vibrations of rings and rolls (*Wülste*) may be found in a forthcoming sequel to those essays.

part imaginary; consequently some groups consist only of one single strong line, and others of a limited number. The more oblate the spheroid, the more prominent is the type. Experimentally the latter is known by the grouping of lines in the spectrum of the metals, gold, silver and copper. Hydrogen too, which in its reactions shows many analogies to metals, belongs to the same class, inasmuch as a thin round plate conceived as an extremely oblate spheroid, shows a spectrum of the same type as hydrogen.

In the third place we will consider the general ellipsoid of three axes, i. e., we will try to find the wave lengths of the light emitted by such an ellipsoid in an incandescent condition. The corresponding lines of the spectrum in this case likewise depend on three numbers, which are determined by transcendental equations and each of which can pass through a certain series of separate values. But these lines are not arranged in series and groups as in the two other instances, but instead are distributed over the whole spectrum. A series can be constructed only when the form of the ellipsoid approaches very near to that of an ellipsoid of revolution. This indeed can be discovered experimentally in the spectrum of the alkaline earths (barium, strontium, calcium and magnesium), i. e., those elements that in their chemical properties stand between alkalis and real metals. The same is true of zinc, cadmium and mercury. The former resemble more closely the prolate ellipsoid; the latter, the oblate.

If we proceed from a spheroid and think of it as varying so gradually that it becomes a general ellipsoid, then the lines of the spectrum will steadily change with the form of the atom, and it follows from the mathematical propositions that out of each individual line eight new ones will appear. Such a splitting of the lines, on the other hand, can be obtained experimentally by bringing the luminous atoms of the element under consideration between the

poles of a strong magnet; this is the well-known Zeeman phenomenon. Between the poles of a magnet the luminiferous ether is in a state of polarization, i. e., in a state of partial tension; but the mathematical treatment of the light-vibrations in polarized ether is the same for a spheroid as that of a general ellipsoid in unpolarized ether. Therefore we can make the inverse statement, viz., that the so-called Zeeman effect, or the splitting of the spectral lines by means of a magnet, is a consequence of the polarization of the ether and takes place as if the atom were correspondingly altered by compression.

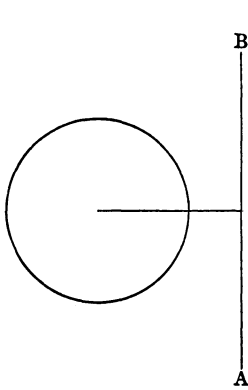


Fig. 2. The circle revolving about the axis A B generates the ordinary ring.

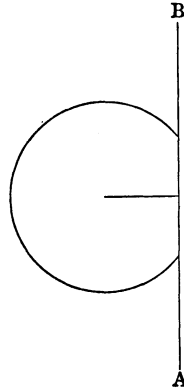


Fig. 3. This circle revolving about the axis A B generates the roll (*Wulst*).

Finally we will take a ring as a possible form of an atom for the basis of mathematical analysis, i. e., such a body as is generated when a circle revolves around an axis which does not pass through its center. We can distinguish two cases:

1. In which the axis does not intersect the rotating circle; the ring is open in the center and has the form of a round wire or rod bent into a circle, in short of a finger ring (Fig. 2);
2. In which the axis intersects the rotating circle; the ring is closed in the center; we speak then of a roll

(*Wulst*); the form is somewhat similar to that of an orange or an apple (Fig. 3).

The vibration problem may still be solved with regard to the ring form although the difficulties are increased; but with it closes the number of forms that can be successfully treated by mathematical methods.

The spectral lines of a luminous ring are dependent on four numbers, each of which must pass through a series of values, and indeed we can most simply get a clear idea of the type of spectrum by repeating several times consecutively the spectrum of a prolate spheroid, while at the same time of course, always shifting somewhat the relative position of the lines in the auxiliary spectrum.

If in the same way the spectrum of an oblate spheroid is repeated consecutively, such a system of spectral lines will be produced as would belong to a luminous roll of the kind above described.

Exactly in this manner Paschen and Runge describe the grouping of the spectral lines in the spectra of oxygen and helium on the one hand, and sulphur and selenium on the other; for according to their view the oxygen spectrum is produced when that of an alkaline metal is shifted repeatedly upon itself; and the sulphur spectrum, when certain groups of lines in the oxygen spectrum are replaced by single heavy lines. So we come to the conclusion that the oxygen atoms are probably in the form of a ring, and the sulphur atoms in the form of a roll.

There is a great fascination in following up the deductions which are connected with these notions and results. First of all it is noteworthy that the *chemical relation* of the elements seems to be dependent on the form of their atoms. Together with attraction and repulsion, the geometrical form of atoms must be considered in relation to the possibility and stability of a combination. So, for

instance, oxides of metals will result when the ellipsoidal metal atoms are deposited in the opening of the oxygen ring and close it up.

The water molecule consists of one atom of oxygen and two atoms of hydrogen; the latter we already know

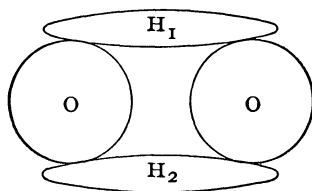


Fig. 4. Cross-section of a water molecule H^2O (one ring cut in two places O, O, and two oblate spheroids, H_1 , H_2).

to be thin round plates. Hence when such thin plates take their places above and below the opening of the ring as it lies in a horizontal position, a water molecule is the result. Analogous to this is the construction of a sulphurated hydrogen molecule, for the roll of a sulphur atom exhibits a depression above and below in which a hydrogen atom can fit itself.

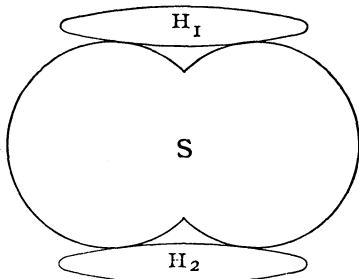


Fig. 5. Cross-section of a molecule of sulphurated hydrogen, H^2S (one roll S, and two oblate spheroids, H_1 , H_2).

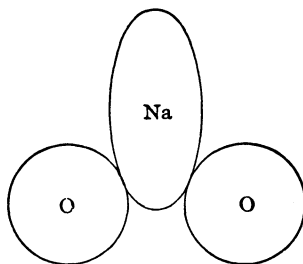


Fig. 6. Cross-section of a molecule of NaO (one ring cut in two places, O, O, and one prolate spheroid, Na).

Now the hydrogen atom may be replaced in every case by an ellipsoidal metal or alkali atom, which substitution would produce hydroxides and oxides, or on the other hand, metallic sulphides (for instance H^2S as shown in Fig. 5). But replacing one of the hydrogen atoms by a

sodium atom, there is no room left for a second sodium atom; consequently an oxygen ring can be combined with one sodium atom only (Fig. 6), and so one sodium (or alkali) atom is able to replace two hydrogen atoms. Under favorable conditions higher degrees of oxidation are formed while oxygen atoms again fix themselves upon the two metal atoms which then in turn offer free cavities for the union with still other metallic atoms.

According to this view, so-called atomicity is dependent on the form of the atom. Atomicity with reference to hydrogen (more generally with reference to ellipsoids) must be distinguished from atomicity with reference to oxygen (more generally with reference to rings). The former is equal to the number of the cavities of the atoms where an ellipsoidal atom may be joined, and the latter is equal to the number of prominences or convexities to which a ring can be affixed.

It would be of especial interest to study the chemistry of carbon combinations from this point of view. First would arise the question of the form of a carbon atom. Its spectrum throughout its entire extent is traversed almost uniformly by spectral lines, whence it is impossible to establish empirically any conformity to law and the mathematical treatment can therefore be of no service. Hence the question must be reversed, and the form of the carbon atom must be determined from the chemical nature of carbon combinations with other elements. This is a path which, as far as carbon is concerned, chemists have pursued under the leadership of Le Bel, van't Hoff and Werner, although with the other elements (with the exception of nitrogen) the question of atomic forms has not heretofore been raised. By this means organic chemistry has succeeded in essentially facilitating clearness of order and distinction in the endless variety of carbon combinations.

Different propositions have been made to so determine the form of the carbon atom that an explanation of the so-called isomeric combinations might be especially derived from it. Whether these propositions are consistent with the notion of atomicity here developed, whether they are not rather obliged to be modified or supplemented, cannot be discussed here. The question becomes intricate in the first place from the fact that the modern stereochemistry, the task of which is to demonstrate the construction of a molecule from its atoms in space, is satisfied by regarding whole groups of combined atoms as new units. When it shall come to pass that the atomic form of the carbon atoms is not used only as a symbol for the systematic arrangement of observations, but that the molecules of organic chemistry are really constructed in their spatial relations out of the form of all utilized atoms, then it will be necessary again to dissolve into its atoms every group of atoms in a molecule, which forms a definite smaller group. By this means the problem becomes unusually involved and we must be content to simply indicate it here.

By such a construction of the molecule a well-defined location within it is assigned to each atom, although it may retain enough freedom to be able to vibrate in this place around a particular point of equilibrium. We must, however, disregard the widely circulated notion that the individual atoms of a molecule describe definite paths around particular centers according to which each molecule would represent a miniature planetary system. This notion has been invented to justify the actual existence of an "internal energy" of the molecule from a mechanical point of view. This internal energy according to the theory here submitted, consists in the internal vibrations of the atoms which serve only in part as outward radiating beams of light, while others make their influence felt

as electrical or magnetic radiation, and at the same time repelling or attracting, so that they have an essential influence on all reciprocal action of atoms. Inasmuch as we treat of the so-called individual vibrations, i. e., of such as are transmitted without any discontinuity from the inside of the atom outwards to the luminiferous ether, the mathematical treatment teaches us that they can only spread simultaneously from the inside outward, and from the outside inward, and that whatever internal energy is lost will always be replaced from without, the luminiferous ether restoring this energy spontaneously. While this exchange of vibrations usually is not noticeable in most atoms under ordinary conditions and must first be aroused by warmth or by electrical energy from without, in the case of other elements (as radium, thorium, etc.) this exchange seems to proceed with extraordinary activity under customary conditions.

In another way the so-called electron theory undertakes to account for the internal energy of molecules. This takes for granted that a large number of electrons are bound up with every material atom; these electrons themselves are neither matter nor luminiferous ether, but a third something—electricity. This notion in addition to the laws of the transposition of ions has arisen from the practice of electrolysis and is based especially upon the remarkable phenomena of radiation displayed in the inside of Geisler tubes, particularly on the observation of the cathode rays. Often the electrons are looked upon directly as the ultimate atoms (*Uratome*) of which matter is essentially composed, the electrical forces dissipating atoms into these ultimate atoms whose paths then become the cathode rays. The lines of the spectrum are thus said to be generated by periodical vibrations of those electrons around certain points of equilibrium, while according to other views each electron has its own definite motion and

with it a definite spectrum whereby the number of lines in the spectrum would be equal to the number of electrons that are combined with the atoms of matter. At any rate a mathematical exposition of empirically determined laws in regard to the grouping of the spectral lines has never yet been attained on the basis of such hypotheses. In explanation of electrical phenomena this theory fulfills its purpose in many respects; as regards the cathode rays it does not contradict the views here submitted concerning the fixed character of atomic forms, for there is no reason why an atom of a particular form under suitable circumstances might not be separated into still smaller particles. What is really remarkable then is only the fact that the ultimate atoms can be accurately reconstructed; that after the electrical disturbance has ceased the original atom is formed again. The further pursuit of these remarks would lead too far into the theory of electricity for us to be able to engage in it now. It only remains to observe that the facts on behalf of the electron theory are also consistent with the hypothesis of atoms of definite formation. Indeed the admission that there are elastic vibrations within the atom is consistent with the notion that the atoms are in their turn composed of smaller particles which periodically change their relative positions by vibrations.

Our investigations have brought us to the point where the problem of the qualitative distinction between chemical elements is reduced to a mathematical problem of form and number in a series of instances. The individual element is characterized by the lengths of the three axes of the ellipsoid which represents the atom, or by the numbers which define the size and form of a ring or roll. Still unexplained, however, is the further question as to why only certain fixed groups of numbers come under consideration, only as many groups as there are different

elements with ellipsoidal or ring-shaped atoms. Why can we not choose these axis lengths and other determining quantities at will, and then assign to them the corresponding elements? Or in short, why is there only a limited number of elements? Why are the intervening links lacking?

Natural forces must exist which are still unknown to us and which operated decisively in the construction of atoms, perhaps are still operating uninterruptedly to-day, to preserve the atoms in their permanent forms or perhaps to prevent possible deflections and variations. This is quite analogous to that other question why only a definite limited number of living organisms exist or are capable of existing. We know that the struggle for existence and the survival of the fittest exercised a conspicuous influence on the formation and preservation of organisms; may not analogous considerations also govern inorganic nature? May not the existing elements have been forming themselves in preference to other eventual possibilities, just because they were best suited to their available external conditions?

These are questions which at present we can scarcely clothe in a mathematical garb. Much less are we able to furnish a solution until we succeed in so shifting the borderline of our understanding as to reduce the qualitative attributes of matter to quantitative differentiations. We may only trust that the future will dissolve and clear away the doubts that still remain.

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